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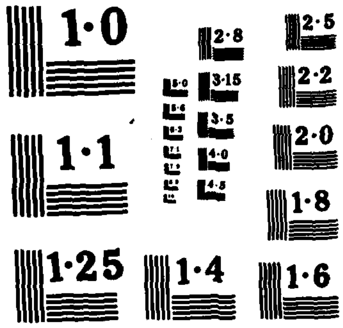
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ATTENUATED TOTAL REFLECTION METHOD FOR OBTAINING OPTICAL CONSTANTS OF POWDERS

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An apparatus designed to measure the optical constants of a powder suspended in a liquid is described. A laser source (3.391 m) and attenuated total reflection approach are used. The accuracy of the apparatus is evaluated by comparing measured results for a liquid hydrocarbon to published results obtained for a carbon black powder are discussed and compared to previously published results from specular reflection measurements. The applicability of the Maxwell-Garnett effective medium theory is considered.

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PREFACE

The work described in this report was authorized under Contract Nos. DAAK11-82-K-0013 and DAAG29-79-C-0130. This work was started in September 1980 and completed in June 1983.

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This report has been approved for release to the public.

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ATTENUATED TOTAL REFLECTION METHOD FOR OBTAINING OPTICAL CONSTANTS OF POWDERS

1. INTRODUCTION

The attenuated total reflectance (ATR) method is one of several techniques available for determining the optical properties of materials. It has proven to be particularly valuable for the study of otherwise intractable problems, for example, highly absorbing materials. The method, known since its presentation by Fahrenfort,[1] has been used successfully by spectroscopists as a complement to standard absorption and reflection techniques. In those applications, an ATR attachment is mounted in a spectrometer having a broad band source of radiation. More recently reports of ATR methods using laser sources have appeared. The desirable properties of lasers have resulted in measurements with improved accuracy and sensitivity, and have allowed for the undertaking of problems which were previously considered impractical.

We have been interested in measuring the infrared optical constants of powders, particularly highly absorbing powders, and have previously reported the results of specular reflection measurements on a series of black powders.[2] In this work we describe an apparatus used to measure the complex refractive index of a carbon black powder at a wavelength of 3.391μm, and the results obtained. We demonstrate the accuracy of the method by comparing measured optical constants of a liquid hydrocarbon with published results obtained using a different method. Also, we show that the Maxwell-Garnett theory for a composite system can be applied to our measurements.

2. EXPERIMENTAL DETAILS

2.1 Background.

The use of ATR methods to determine infrared optical constants has been reviewed by Crawford, Goplen and Swanson.[3] Briefly, we are interested in the reflectance of radiation at a boundary separating a lossless solid (crystal) from a lossy liquid (sample). If the light approaches the boundary from the lossless medium, the reflected beam will penetrate the sample to a depth approximately equal to the wavelength. This penetrating wave, which is damped exponentially, is called the evanescent wave. The reflectance of this probing wave depends upon the optical constants of the crystal n_1 and sample $n^*_2 = n_2 - ik$, where k is the absorption coefficient, and the angle of incidence.

The optical behavior at the boundary also depends upon the polarization of the radiation. If θ is the angle of incidence at the interface, the reflectance R_s for radiation polarized perpendicular to the plane of incidence is

$$R_s = 1 - \frac{4a\cos\theta}{[a^2 + G + (a + \cos\theta)^2]} \tag{1}$$

where

$$a = \{[(G^2 + 4k^2N^4)^{\frac{1}{2}} - G]/2\}^{\frac{1}{2}} \tag{2}$$

$$G = \sin^2\theta - N^2(1 - k^2) \tag{3}$$

and

$$N = n_2/n_1 \tag{4}$$

These equations, as well as those to be given below, have been given by Hirschfeld.[4] The parallel component of the reflectance R_p is given by

$$R_p = R_s \left[1 - \frac{4a \sin\theta \tan\theta}{a^2 + G + (a + \sin\theta \tan\theta)^2}\right] \tag{5}$$

Equations (1) through (5) allow us to obtain the optical constants n_2 and k from measurements of θ, R_s and R_p. An algorithm for extracting n_2 and k from the measured quantities is as follows:

$$n_2 = n_1 \{[(X^2 + 4Y^2)^{\frac{1}{2}} + X]/2\}^{\frac{1}{2}} \tag{6}$$

$$k = \{[(X^2 + 4Y^2)^{\frac{1}{2}} - X]/2Y\} \tag{7}$$

where

$$X = 2a^2 - (F_s + F_p)/2 + (1 + \tan^2\theta)/2 \tag{8}$$

$$Y = a[(aF_s - a^2 - \cos^2\theta)(aF_p - a^2 - \sin^2\theta \tan^2\theta)]^{\frac{1}{2}} \tag{9}$$

and

$$a = (1 - \tan^2\theta)/(F_s - F_p) \tag{10}$$

$$F_s = 2 \cos\theta (1 + R_s)/(1 - R_s) \tag{11}$$

$$F_p = 2 \sin\theta \tan\theta \frac{(1 - R_p/R_s)}{(1 + R_p/R_s)} \tag{12}$$

It has been pointed out by Hirschfeld,[4] that the above algorithm is sensitive to round off errors and that the method cannot be used when the angle of incidence is near 45°. This will be seen in results presented below.

Researchers[4,5] have evaluated the accuracy and limitations of several different techniques which utilize the ATR method. The technique chosen here requires a single prism. It has the advantage of being simple to use although it is less accurate than some of the other techniques.

Figures 1 and 2 are plots of R_s and R_p versus θ, generated using the above equations, for $n_1 = 4.034$ (germanium) and $n_2 = 1.500$ (approximate value for our samples). The absorption coefficient has been varied from k = 0 to k = 1.00 in steps as shown. As expected, for a lossless sample (k = 0) both reflectances rise to 1.00 at the critical angle θ_c (here 21.83°) and remain there for $\theta_c \leq \theta \leq 90°$. For $k \neq 0$, the reflectance curves change with k.

2.2 Apparatus.

Figure 3 is a schematic diagram of the apparatus constructed. Radiation from a Spectra Physics Model 120 HeNe Laser L_1 (3.391μm output only) is chopped at 9.3Hz, directed into and out of a germanium prism by mirrors M_1 and is detected by a Molectron P1-72 pyroelectric detector. The detector signal is amplified using a Princeton Applied Research Model 128A lock-in amplifier and displayed on a Leeds and Northrup strip chart recorder. The germanium prism, isosceles with prism angle of 140°, is mounted in a goniometer which allows angular positioning to an accuracy

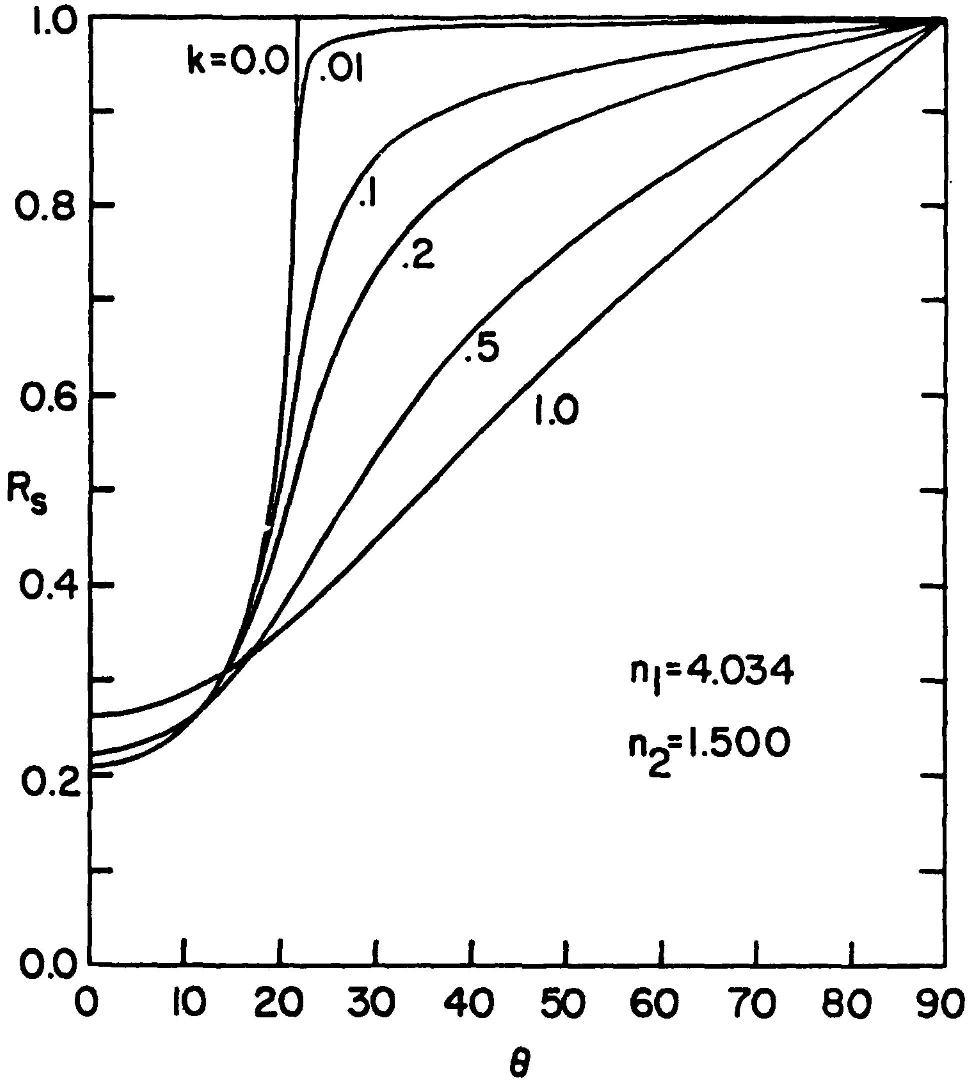


Figure 1. Perpendicular Reflectance Versus Angle of Incidence Curves for Various Values of Extinction Coefficient
Critical Angle is 21.83°

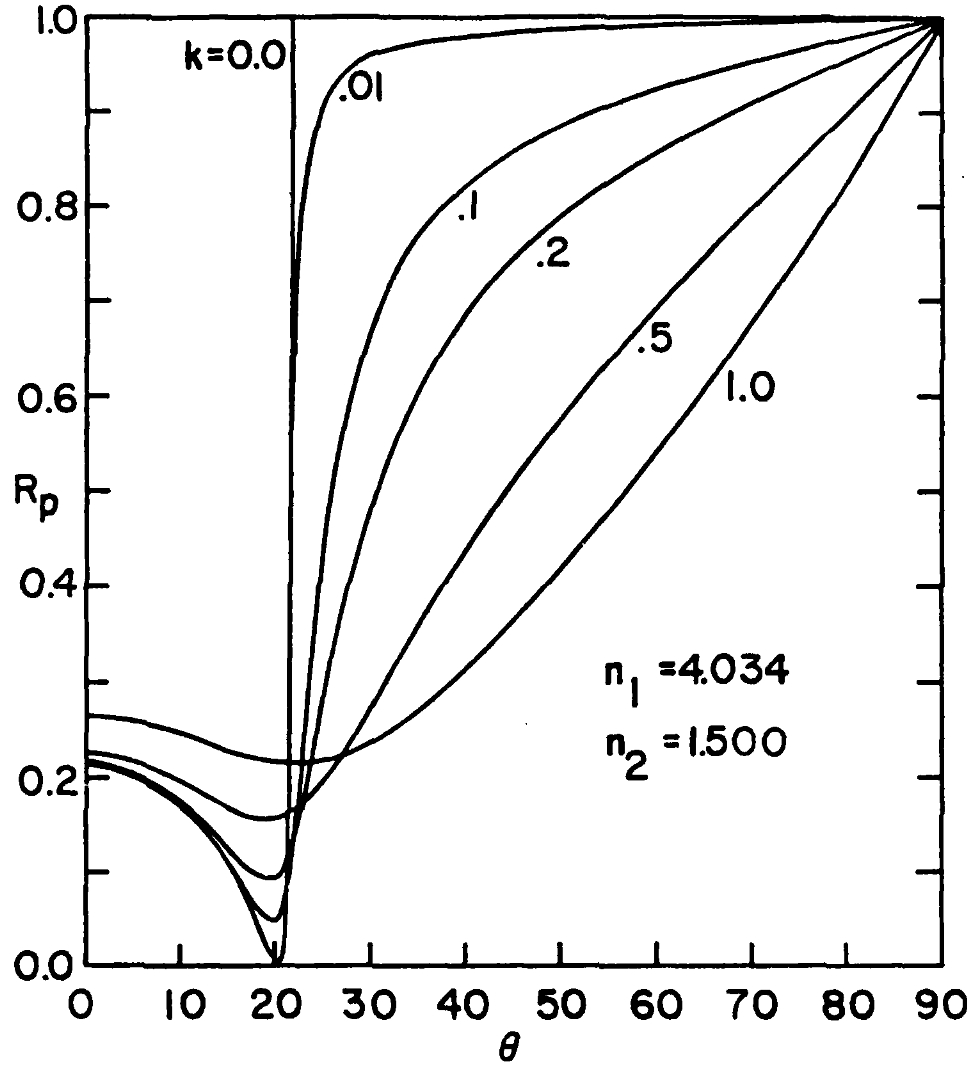
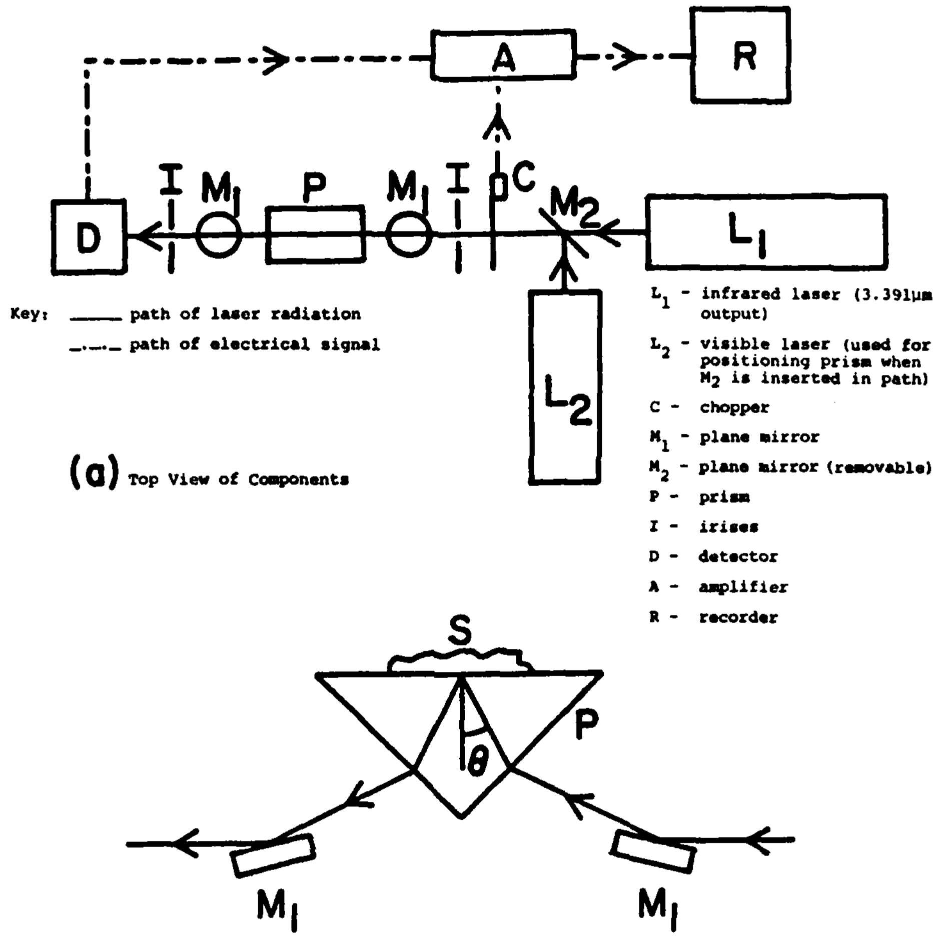


Figure 2. Parallel Reflectance Versus Angle of Incidence Curves for Various Values of Extinction Coefficient Critical Angle is 21.83°



(b) Side View of Prism Showing Sample S and Path of Laser Beam

Figure 3. Schematic diagram of apparatus used to make ATR measurements

of between 0.05° and 0.20°, depending upon the angle used. The interface between the germanium prism and sample to be studied is in the horizontal plane, so that liquid samples may easily be studied.

A visible HeNe laser L_2 (Spectra Physics Model 155) is used to align the optical components and set the desired angle of incidence when the removable mirror M_2 is introduced as shown in Figure 3. The infrared laser (L_1) is mounted in a cradle which rotates about an axis which is colinear with the beam axis. The output beam of this laser is polarized to within one part in one thousand. Rotation of the infrared laser about its longitudinal axis therefore allows radiation having either polarization direction to reach the prism-sample interface.

The reflectance values are determined by reading the strip chart deflections with and without the samples on the prism interface and ratioing the resulting numbers.

2.3 Evaluation of Apparatus and Method.

As a check on the performance of the apparatus and accuracy of the method, we have measured the optical constants of toluene. Toluene was selected as a test material because it has an absorption band at a wavelength very near to the wavelength of the laser line, and thus has a reasonable absorption coefficient k, and because accurate and reliable published values of n and k are available in the literature for comparison. The choice of a liquid for evaluation is obvious since the surface contact problem is not a factor.

Since the measured quantity in this method is a reflectance, we have presented the results in terms of $R_p(\theta)$ and $R_s(\theta)$. Goplen, Cameron and Jones[6] have reported the results of very careful measurements on a number of organic liquids. Their measurements were made with a grating spectrophotometer using transmittance methods. We have used their published values of n_2 and k measured at 2949cm^{-1} (3.39 μm), along with n_1 for germanium to calculate $R_s(\theta)$ and $R_p(\theta)$. The results are plotted in Figure 4 as solid lines, and are taken to be the reference values. The open circles in Figure 4 represent our measured data for toluene on a germanium prism. The agreement is quite good.

The optical constants obtained by Goplen, Cameron and Jones for toluene at 3.39 μm are $n = 1.4741$ and $k = 0.00962$. The corresponding values we obtained are $n = 1.484$ (measured at 19°) and $k = 0.015$ (measured at 23°). The angles chosen for the measurements were selected on the basis of our error analysis (see below). Our results differ from those of Goplen, Cameron and Jones by 0.7% and 44.0% respectively. A 44% error in absorption coefficient might appear to be excessive. However, it is approximately the error predicted by an error analysis for a sample with $k = 0.01$. By comparison, the samples of interest to us in this study have an absorption coefficient $k \simeq 0.2$. According to our error analysis, we should realize errors in k on the order of a few percent for these samples.

2.4 Samples.

The objective of this study was to obtain the infrared optical constants of black powder using the ATR method. Transmission measurements on dispersed powder samples are limited in accuracy by low transmittance values and, hence, low signal-to-noise levels. Typical particle loadings (concentration of powder in transparent host medium) for black powders tested spectrophotometrically are limited to about 2-5% by weight.

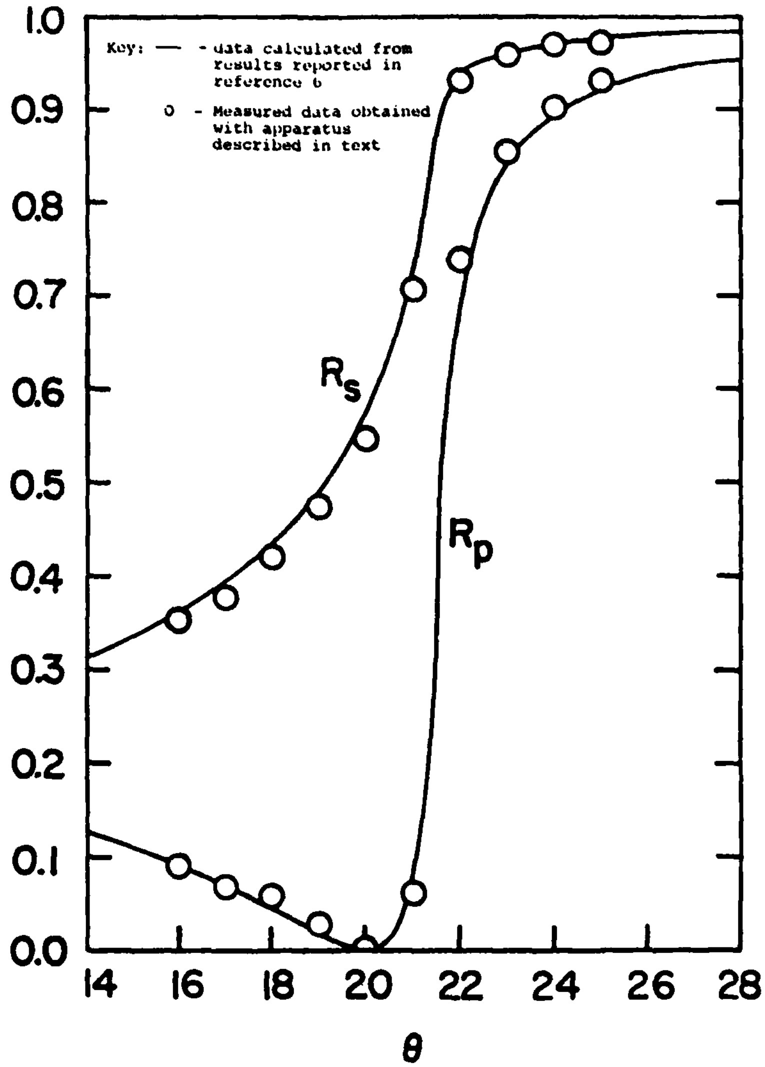


Figure 4. Reflectance Curves for Toluene

Reflection measurements on compacted pure powder pellets are possible, but reflectances are also low and the method is subject to other considerations.[2] The ATR method used with a laser source should not be limited by the above problems and should therefore offer some advantages. The primary limitation in this method is poor contact between particulate sample and prism. However, this problem may be circumvented by suspending the powder in a liquid of known, or measurable, optical properties. The surface contact between liquid-powder mixture and prism is then satisfactory and the optical constants of the powder sample can be extracted from those of the mixture.

The powder sample investigated in this study was a carbon black (Mogul L, Cabot Corp., Boston, MA). The manufacturer's stated average particle size for this powder is 0.024μm, but agglomeration effects most certainly results in larger sized clusters. The carbon black powder was mixed with nujol oil, a refined liquid paraffin commonly used by spectroscopists to prepare mull-type samples. The nujol was convenient to use, non-volatile, reasonably pure, and viscous enough to prevent settling out of the carbon black particles during the measurement time. Mixtures of Mogul L and nujol were prepared with weight fractions of carbon black from 0 to 50%. Starting with a loading of 40% carbon black, the viscosity of the mixture was such that surface contact problems were encountered. At 50% concentration, the mixture was more paste-like than liquid. No higher concentrations were attempted.

2.5 Error Considerations.

A method of error analysis, similar to that given by Hirschfeld,[2] was used here to determine the angle of incidence which would yield the least error in n_2 and k. Values of $n_1 = 4.034$ (germanium), $n_2 = 1.500$, and various values of k and θ were used to generate the reflectance values, R_s and R_p. R_s, R_p and θ were then varied as follows: $\Delta R = \pm 0.01$, $\Delta\theta = \pm 0.20°$. These variations in R and θ were chosen to be representative of the experimental limitations of the apparatus. The varied R_s, R_p and θ values were substituted into the algorithm to obtain n'_2 and k', the varied optical constants. Finally, the errors $(n'_2 - n_2)/n_2$ and $(k' - k)/k$ were calculated and plotted as a function of θ. The results are shown in Figures 5 and 6 for several values of the absorption coefficient k. The powder suspensions used in this study had k values of about 0.1 - 0.2. Consequently, the optimum values of the angle of incidence used, based upon Figures 5 and 6, were between 22° and 25°.

2.6 Experimental Results.

Figures 7 and 8 present the results of the ATR measurements on the carbon black suspensions. The values of n and k are given for $0 \le f_w \le 0.50$, where f_w is the weight fraction of carbon black. For each sample weight fraction, a minimum of 2 reflectance measurements were made for each polarization direction. The optical constants derived from various combinations of R_s and R_p values were averaged to obtain each data point shown. Deviations from the average values are indicated by the error bars. Note that the scales are not equivalent in Figures 7 and 8 so that the indicated error bars can be misleading. For example, at $f_w = 0.30$, $\Delta n/n = 1.3\%$ whereas $\Delta k/k = 9.7\%$.

The refractive index values appear to increase linearly with f_w. A linear regression analysis of the data points gives a correlation coefficient of 0.997. The absorption coefficient data in Figure 8 by comparison, do not suggest a linear increase of k with f_w, but, such a trial linear fit produced a correlation coefficient

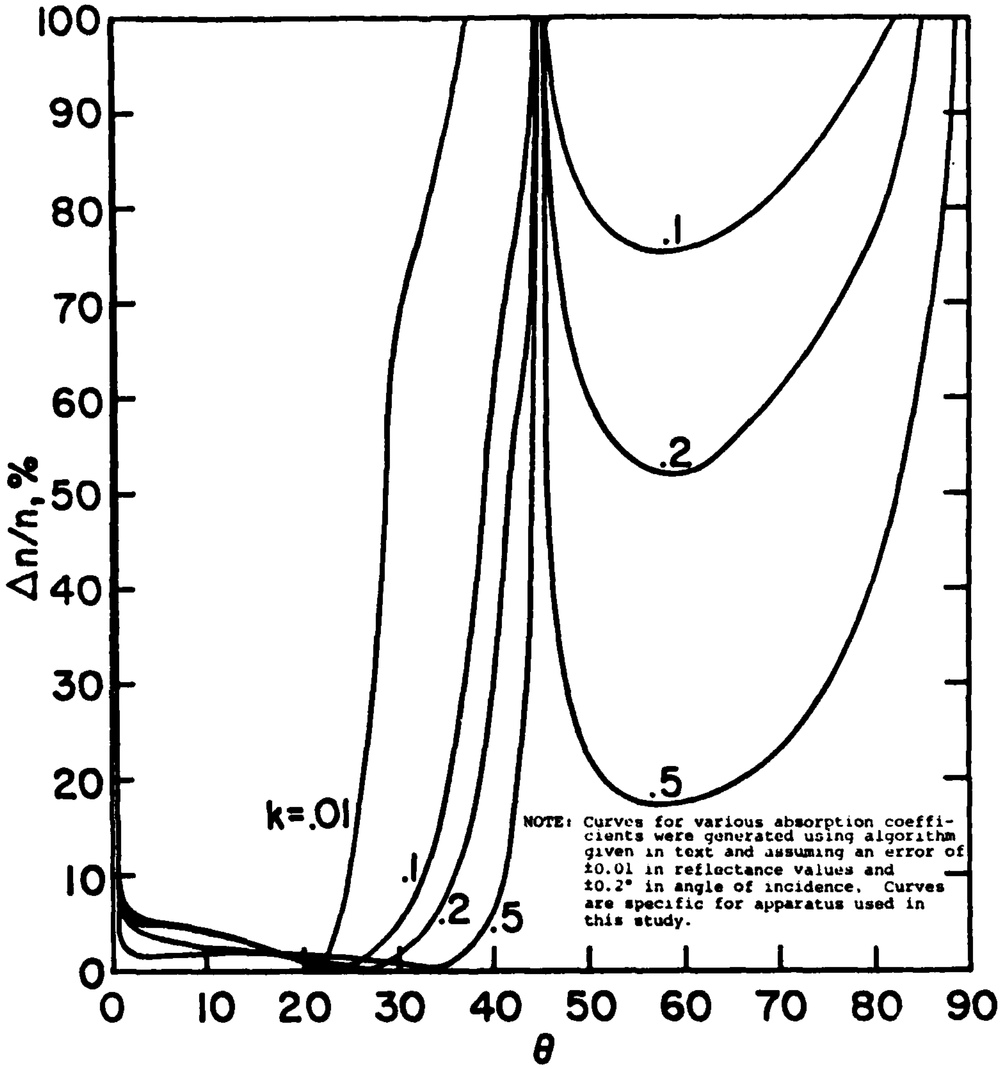


Figure 5. Calculated Error in Index of Refraction

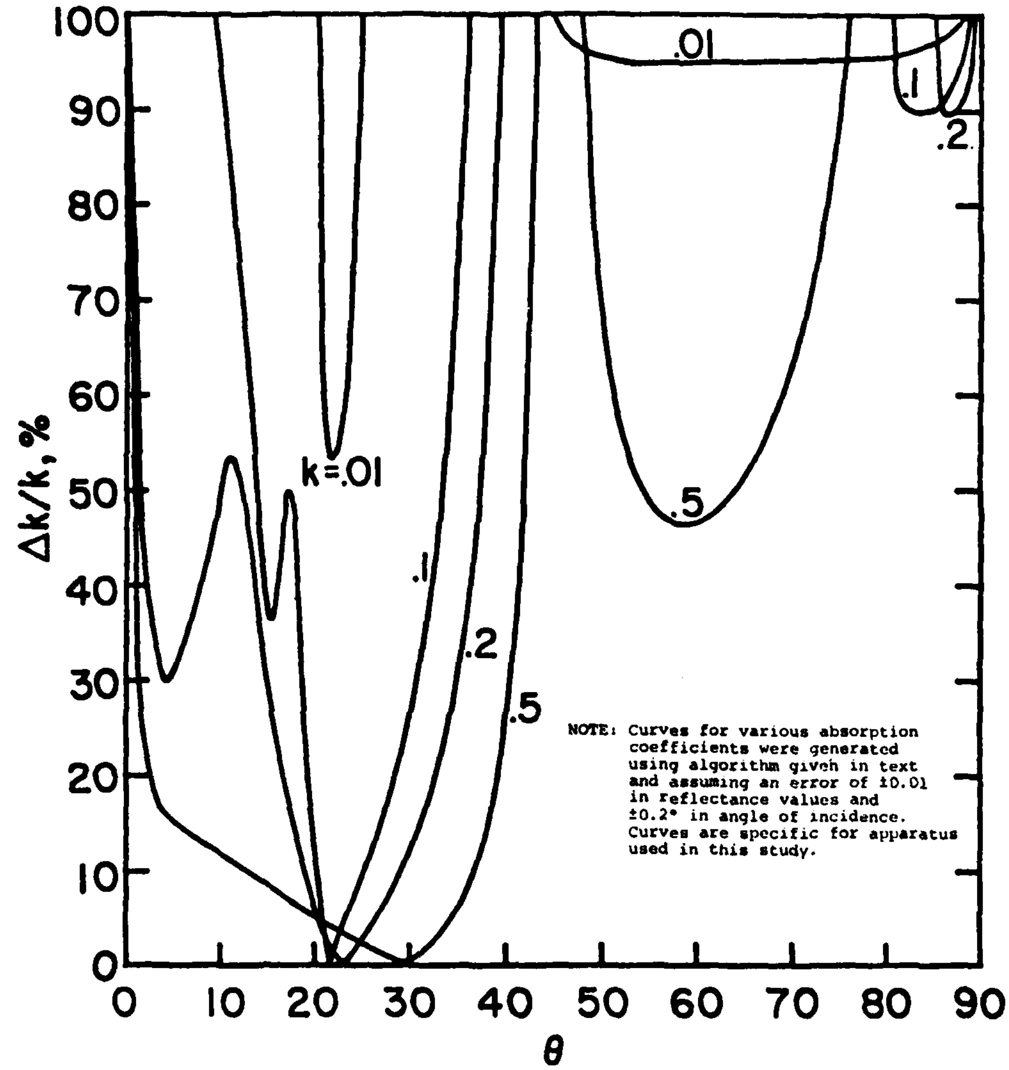


Figure 6. Calculated Error in Absorption Coefficient

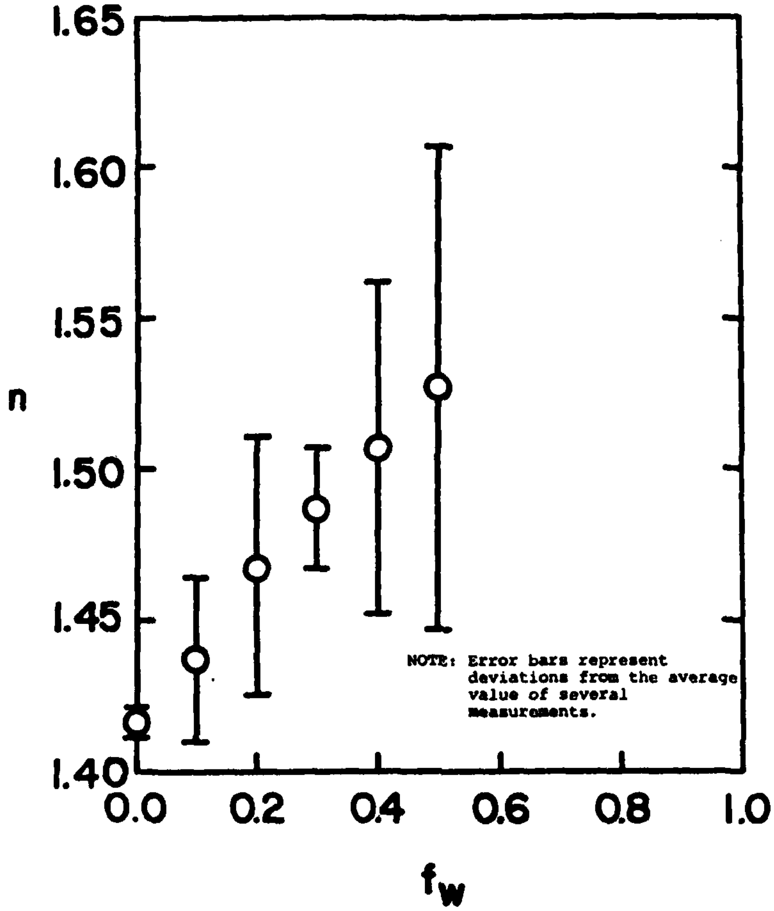


Figure 7. Index of Refraction of Mogul L Carbon Black Suspension as a Function of Weight Fraction of Powder in Host Material

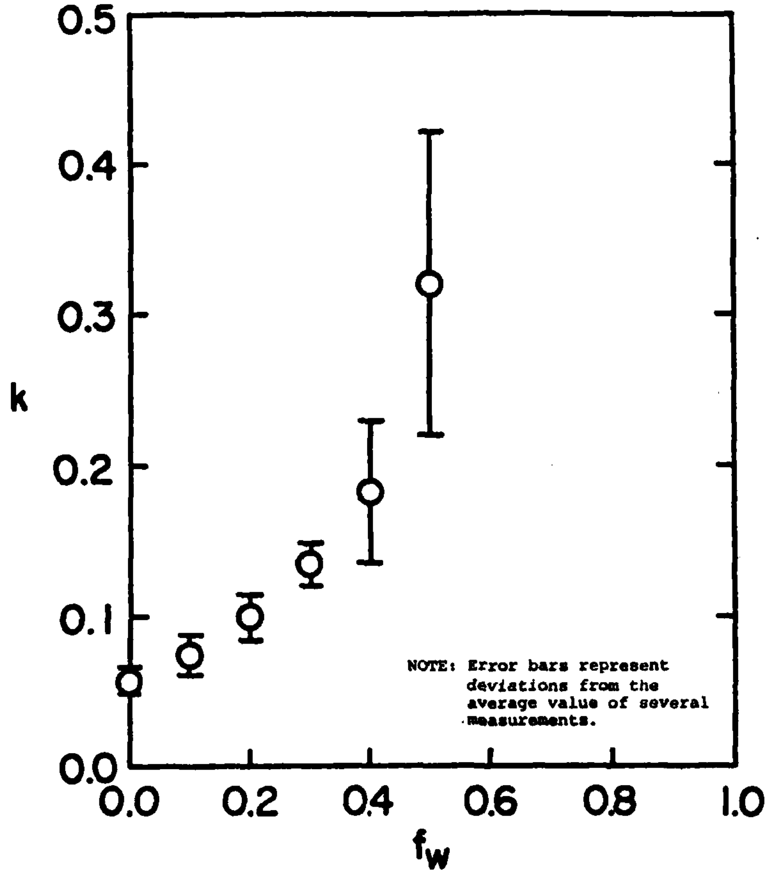


Figure 8. Absorption Coefficient of Mogul L Carbon Black Suspension as a Function of Weight Fraction of Powder in Host Material

of 0.923. As will be seen below, this behavior is expected for components with similar permittivities. Assuming that the linear relationships hold for all values of f_w up to unity, the optical constants for the pure powder can be obtained by a linear extrapolation. The results, together with values previously obtained, are presented in the following table.

2.7 Discussion.

A correct extrapolation of measurements made on a mixture to the case of the pure powder, requires the use of a mixture rule or effective medium theory. Such mixture rules are generally formulated in terms of the permittivity, also a complex quantity. The connections between the permittivity $\varepsilon^* = \varepsilon' - i\varepsilon''$ and index of refraction $n^* = n - ik$ is given by the relations

$$\varepsilon = n^2 - k^2 \tag{13a}$$

$$\varepsilon'' = 2nk \tag{13b}$$

The simplest effective medium theory, proposed by Maxwell-Garnett,[7] is obtained from the ratio of the volume averaged electric displacement to the volume averaged electric field. The result is

$$\varepsilon_{12} = \varepsilon_2 \left[1 + \frac{3f_v\ (\varepsilon_1 - \varepsilon_2)}{(1 - f_v)\varepsilon_1 + (2 + f_v)\varepsilon_2}\right] \tag{14}$$

where ε_{12}, ε_1, and ε_2 are the permittivity magnitudes of the effective medium, suspended component and host medium respectively, and f_v is the volume fraction of medium 1. Equation (14) is strictly valid only for small values of f_v (dilute mixtures) and for spherical particles whose diameters are smaller than the wavelength. It can be easily shown that if $|\varepsilon_{12}| \approx |\varepsilon_1| \approx |\varepsilon_2|$, then both ε_{12} as well as n_{12} and k_{12} depend linearly on f_v.

We have analyzed our optical data in terms of the Maxwell-Garnett model. Figure 9 is a plot of ε_{12} versus f_v for Mogul-L carbon black. The solid line was generated by using Equation (14) for arbitrary values of f_v but measured values of ε_1 and ε_2. The permittivity ε_2 of the host medium was determined from n and k values obtained using the ATR apparatus described above. The permittivity ε_1 of the suspended powder was calculated from previously measured optical constants of Mogul-L determined from specular reflection measurements on pressed pellet samples,[2] using Equations (13a) and (13b). Thus the solid line represents a calculated or predicted permittivity of the effective medium based upon the Maxwell-Garnett model. The five data points shown in Figure 9 are for our measured data obtained from various carbon black/nujol mixtures and calculated from Equations (13a) and (13b). Weight fractions were converted to volume fractions, using a density of Mogul-L ($1.25 gm/cm^3$) measured in our laboratory. This density value is different from the apparent density quoted by the manufacturer[8] ($0.240 gm/cm^3$) or that found in the literature for carbon blacks ($1.86 - 2.04 gm/cm^3$).[9]

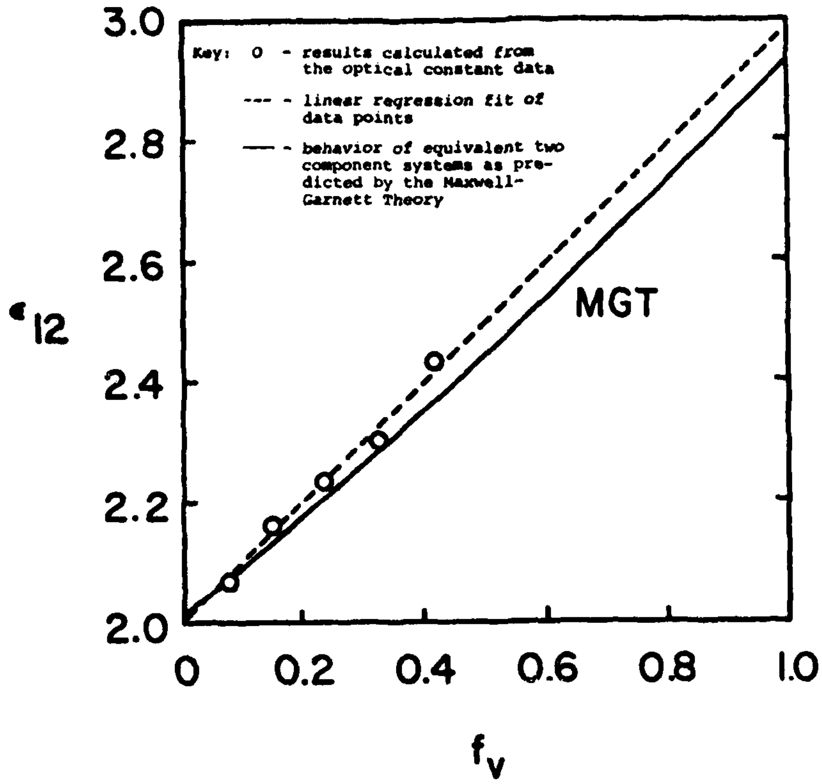


Figure 9. Permittivity of Mogul L Carbon Black Suspension as a Function of Volume Fraction of Powder in Host Material

Optical Constants of Mogul L Carbon Black Powder

at 3.391μm

	Extrapolated from ATR measurements on powder suspensions; this work	Determined from specular reflection measurements on pressed powder pellets; reference 2	Per cent difference
n	1.64	1.57	4
k	0.50	0.68	31

The results of Figure 9 show that our measured values of ε_{12} are in very good agreement with the values predicted from the Maxwell-Garnett theory (MGT). The MGT curve exhibits slight curvature and has a pure powder ($f_v = 1.0$) value of 2.93. A linear regression analysis of the measured data points, including the $f_v = 0$ point, yields good fit (correlation coefficient of 0.996) and a pure powder extrapolated value of $\varepsilon = 2.99$. These two permittivity values differ by about 2%.

As mentioned earlier, the linear behavior of ε_{12} on f_v is not unexpected since for our materials $|\varepsilon_{12}| \approx |\varepsilon_1| \approx |\varepsilon_2|$. For larger differences between ε_1 and ε_2, the linear approximation becomes progressively less accurate. This explains why, in Figures 7 and 8, both $n(f_w)$ and $k(f_w)$ could be represented by a linear fit with high correlation coefficients (0.997) and 0.923 respectively).

The fact that the carbon black particles are probably not spheres and that relatively high volume fractions were used appear not to have a noticeable influence on the results. Depending upon the grade of material, carbon blacks are produced with a particle size in the range of 10 to 300 μm. Fusing and agglomeration results in primary aggregates of random size and shape. Mixing and sample handling may reduce agglomeration effects slightly, but the condition of small spherical, and isolated particles, assumed in the theory, is very probably not met. Very recently, Niklasson and Craighead[10] have measured the optical properties of aluminum-silicon films and analyzed their reflectance data in terms of effective medium theories. Even though electron micrographs of their films showed the presence of non-spherical particles, they obtained good agreement between their measurements and results evaluated from two effective medium theories.

In another recent work, Jennings[11] used the ATR method with a CO_2 laser source to obtain the optical constants of aqueous suspensions of polystyrene spheres. Also using MGT, Jennings investigated suspensions up to a 30% weight fraction of polystyrene, hardly the realm of dilute mixtures. The polystyrene particles used here, however, were spherical and much smaller than the radiation wavelength.

In summary, the optical constants of a carbon black powder were obtained from ATR measurements on a mixture of the powder and a suitable host material. The results are in good agreement with data obtained from previous measurements using a different technique. The MGT provides a surprisingly good representation of the data, considering the nature of the sample. The method yields reasonably accurate and reproducible results provided the experimental conditions and parameters are carefully chosen and maintained.

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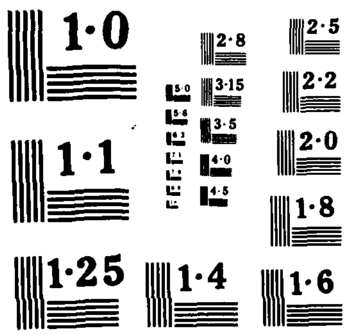
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